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13. ABSTRACT *(Maximum 200 words)*

The primary objective of this project was to study the processing and high-temperature deformation of laminated Nb/Nb5Si3 composites. Our initial goal was to control the grain size and porosity present in the Nb5Si3 silicide phase of the composites by developing improved processing techniques. For this part of the project we investigated four processing routes including hot pressing during annealing, vapor deposition onto a heated substrate, annealing under a large thermal gradient, and hot pressing elemental Nb/Si microlaminates. The final processing method proved most promising and demonstrated that full dense Nb/Nb5Si3 microlaminates can be processed with large grains and no metastable phases. Our subsequent goal was to characterize the deformation of Nb/Nb5Si3 microlaminates at high temperatures and determine the controlling deformation mechanisms in both phases. We demonstrated that the creep rate of the silicide phase at 1000°C and 1100°C has a nonlinear dependence (or weak power law dependence) on stress and a very strong dependence on grain size, larger than the 1/d3 dependence expected for Coble creep, which is the predicted deformation mechanism at these temperatures and stresses (10-100MPa). For the Nb phase at 600°C power law creep is observed under high stresses with no grain size dependence, as expected. Under lower stresses, diffusional creep is observed, also as expected. However, unlike conventional diffusional creep, this data set shows a weak, 1/d, grain size dependence and an approximately linear stress dependence (1.0). The data support an earlier hypothesis that the rate of vacancy generation and annihilation controls diffusional creep in fine-grained samples, not the rate of vacancy diffusion.

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PROCESSING AND HIGH TEMPERATURE PROPERTIES OF Nb/Nb_5Si_3 LAMINATES

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Final Report

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1.0 Executive Summary: Research Objectives and Accomplishments

The primary objective of this project was to study the processing and high-temperature deformation of laminated Nb/Nb_5Si_3 composites. Our initial goal was to control the grain size and porosity present in the Nb_5Si_3 silicide phase of the composites by developing improved processing techniques. Our subsequent goal was to characterize the deformation of Nb/Nb_5Si_3 microlaminates at high temperatures and determine the controlling deformation mechanisms in both phases.

In the first half of the project we focused primarily on manufacturing high quality Nb/Nb_5Si_3 microlaminate foils in order to determine the predominant creep mechanisms in these materials in the second half. We were concerned specifically with manufacturing a series of fully dense microlaminates with average grain sizes ranging from a fraction of a micron to tens of microns in order to determine the importance of Coble creep in these materials.

Previously we manufactured Nb/Nb_5Si_3 microlaminates by sputter depositing alternate layers of Nb and Nb_5Si_3 onto an unheated substrate, but we were not able to produce fully dense silicide layers with micron scale grain sizes. Anneals at high temperatures (1600°C) lead to Si loss, porosity, and metastable phase formation. Thus we investigated several new processing routes including:

1. Hot pressing during annealing: The addition of pressure suppressed porosity and metastable phase formation but did not achieve significant grain growth.
2. Vapor deposition onto a heated substrate: The heating of substrates to 300°C, 400°C and 600°C did not produce crystalline silicide layers, and technical limitations prevented the use of higher temperatures.
3. Annealing under a large thermal gradient: using an image furnace in collaboration with Dr. Ian Baker at Thayer School of Engineering we found no significant

increase in the grain size of the silicide phase over conventional processing routes.

4. Hot pressing Nb/Si microlaminates: elemental layers of Nb and Si (sheet and vapor deposited) were used in an attempt to minimize impurities and thereby increase grain growth. Grain growth was increased in both cases (up to 8μm) but metastable phases could not be removed and Kirkendall porosity was seen when hot pressing at temperatures up to 1670°C. Hot pressing vapor deposited Nb/Si microlaminates overcame both problems but time limitations and an inability to hot pressing specimens of acceptable length prevented the manufacture of a full set of samples using this method.

In the second half of this project we studied creep rates and creep mechanisms for the silicide phase in Nb/Nb_5Si_3 microlaminates at 1000°C and 1100°C and we studied the creep rates and creep mechanisms for the Nb phase in Cu/Nb microlaminates at 600°C. To summarize, the creep rate of the silicide phase has a nonlinear dependence (or weak power law dependence) on stress and a very strong dependence on grain size, larger than the $1/d^3$ dependence expected for Coble creep, which is the predicted deformation mechanism at these temperatures and stresses (10-100MPa). For the Nb phase power creep is observed at high stresses with no grain size dependence, as expected. At lower stresses, diffusional creep is observed, also as expected. However, unlike conventional diffusional creep, this data set shows a weak, 1/d, grain size dependence and an approximately linear stress dependence ($\sigma^{1.0}$). The data support an earlier hypothesis that the rate of vacancy generation and annihilation controls diffusional creep in fine-grained samples, not the rate of vacancy diffusion.

The current study has shed important light on the processing of metal/silicide microlaminates and on the grain size dependence of creep in Nb_5Si_3 and Nb. The study suggests that the formation of microlaminate samples with large silicide grain sizes could lead to materials with a creep resistance that is superior to the creep resistance of similar cast and extruded alloys. The study also demonstrates the utility of microlaminates as model materials for studying mechanical properties in samples with well-controlled grain sizes. Besides structural materials, these results should also impact the study of deformation in thin films on substrates where steady state creep conditions are rarely achieved.

2.0 Publications, Presentations, and Other Public Dissemination

2.1 Journal Publications:

A. C. Lewis, D. Van Heerden, and T. P. Weihs, *Creep Mechanisms in Fine-Grained Niobium*, Acta Materialia, to be submitted June 2004.

A. C. Lewis, D. Van Heerden, D. Josell, and T. P. Weihs, *Creep Deformation of Multilayered and Microlaminate Materials,* JOM, 55, 34-37, (2003).

A. C. Lewis, D. Josell, and T. P. Weihs, *Stability in Thin Film Multilayers and Microlaminates: The Role of Free Energy, Structure, and Orientation at Interfaces and Grain Boundaries*, Scripta Met. Mat, **48**(8): 1079-85 (2003).

D. Josell, T.P. Weihs, H. Gao, *Diffusional Creep: Stresses and Strain Rates in Thin Films and Multilayers*, MRS Bull., **27**, 39-44, (2002).

D. Van Heerden, A.J. Gavens, P.R. Subramanian, T. Foecke, and T.P. Weihs, *The Stability of Nb/Nb_5Si_3 Microlaminates at High Temperatures*, Metall. Mater. Trans., **32**, 2363-2371, (2001).

C.H. Shang, D. Van Heerden, A.J. Gavens, and T.P. Weihs, *An X-ray Study of Residual Stresses and Bending Stresses in Free-standing Nb/Nb_5Si_3 Microlaminates*, Acta Mater., **48**, 3533-3543, (2000).

D.Van Heerden, A.J. Gavens, T. Foecke, and T.P. Weihs, *Evaluation of Vapor Deposited Nb/Nb_5Si_3 Microlaminates*, Mat. Sci. and Eng. A., **A261**, 212-216 (1999).

A.J. Gavens, D.Van Heerden, T. Foecke, and T.P. Weihs, *Fabrication and Evaluation of Vapor Deposited Nb/Nb_5Si_3 Microlaminates*, Metall. and Mater. Trans., **30A**, 2959-2965 (1999).

2.2 Conference Proceedings:

D. Van Heerden and T.P. Weihs, *The Thermal Stability of Nb/Nb_5Si_3 Microlaminates in Vacuum and Ar*, Structural Intermetallics, edited by K.J. Hemker, D.M. Dimiduk, H. Clemens, R. Darolia, H. Inui, J.M. Laarsen, V.K. Sikka, M. Thomas, and J.D. Wittenberger, TMS (The Minerals, Metals, and Materials Society), 607-613, 2001.

A. C. Lewis, A. B. Mann, D. van Heerden, D. Josell, and T. P. Weihs, *The Effect of Interfacial Free Energies on the Stability of Microlaminates,* Mat. Res. Soc. Proc. 652, 2001.

2.3 Presentations:

Processing and High Temperature Properties of Nb/Nb_5Si_3 Laminates, A. C. Lewis, D. van Heerden, and T. P. Weihs, AFOSR Metals and Ceramics Review, Bar Harbor ME, August 14, 2002.

Creep and Stability of Microlaminate Samples, A. C. Lewis, D. van Heerden, and T. P. Weihs, Gordon Research Conference on Mechanical Properties of Thin Films and Stresses, July 17th, 2002. (Poster)

The Stability and Properties of Metal-Silicide Microlaminates for High-Temperature Applications, A. C. Lewis, D. van Heerden, and T. P. Weihs, ISSI Conference, Jackson Hole, WY, April 2002. (Invited)

Processing and High Temperature Properties of Nb/Nb_5Si_3 Laminates, D. Van Heerden, and T. P. Weihs, AFOSR Metals and Ceramics Review, Snow Bird, UT, August 21, 2001.

Metal-Silicide Microlaminates for High-Temperature Applications: Fabrication, Stability and Properties, D. van Heerden, T. Foecke, and T. P. Weihs, MRS Meeting, Boston, MA, November 25, 2000. (Invited)

The Effect of Interfacial Free Energies on the Stability of Microlaminates, A. C. Lewis, A. B. Mann, D. van Heerden, D. Josell, and T. P. Weihs, MRS Meeting, November 26, 2000.

Processing and High Temperature Properties of Nb/Nb_5Si_3 Laminates, D. Van Heerden, and T. P. Weihs, AFOSR Metals and Ceramics Review, San Diego, CA, October 12, 2000.

Stable Microlaminates and Reactive Nanolaminates for Structural Applications, T.P. Weihs, Case Western Reserve University, Department of Materials Science and Engineering, Cleveland, OH, April 4, 2000. (Invited)

2.4 Other Dissemination:

A.C. Lewis, *The Effect of Interfaces on the Stability and Mechanical Properties of Polycrystalline Multilayers*, PhD thesis, Johns Hopkins University, April 2003.

3.0 Technology Transitions

3.1 Transition of Vapor Processing Skills and Materials to WPAFB:

We worked with Dr. Mike Uchic in the Materials Directorate at WPAFB. In exchange for chemical analysis, we deposited thick copper films on Si wafers to enable his processing of multilayer foils and more importantly, we offered advice and guidance on how to make thick nanolaminates and microlaminates. Dr. Uchic spent time in our research facilities learning how to fabricate such samples.

3.2 Exchange of Data with GE GRC:

We exchanged data with Dr. P.R. Subramanian and Dr. B. Bewlay at GE's Global Research Center. They were particularly interested in the creep data for Nb_5Si_3 that we had generated on microlaminate samples, as a function of grain size at 1100°C.

4.0 Supported Personnel

Timothy P. Weihs, Associate Professor
David Van Heerden, Research Professor
Changhe Shang, Research Associate
Alexis Lewis, PhD Student

5.0 Details of Research Accomplishments

5.1 Processing of Nb/Nb_5Si_3 Microlaminates:

In the first half of the project we focused primarily on manufacturing high quality Nb/Nb_5Si_3 microlaminate foils in order to determine the predominant creep mechanisms in these materials. We were concerned specifically with manufacturing a series of fully

dense microlaminates with average grain sizes ranging from a fraction of a micron to tens of microns in order to determine the importance of Coble creep in these materials.

Previously we manufactured Nb/Nb_5Si_3 microlaminates by sputter depositing alternate layers of Nb and Nb_5Si_3 onto an unheated substrate [1-3]. The Nb_5Si_3 deposited amorphous and was subsequently crystallized by annealing at 1200°C. Although this processing route did produce fully dense Nb/Nb_5Si_3 multilayers with uniform layering and phases, it did have some limitations. The first is that the Nb_5Si_3 grain size cannot be varied significantly in this process method. On crystallization, the Nb_5Si_3 layers have a small grain size (typically 200nm), which increases little on subsequent annealing, unless anneal temperatures approach 1600°C. However, at 1600°C, the microlaminates rapidly loose Si to the atmosphere via surface sublimation [2-3]. The second limitation is that bulk porosity forms in the silicide layers during annealing. The third limitation is that the Nb_5Si_3 layers tend to have high impurity levels. TEM examination of the crystallized Nb_5Si_3 layers revealed that silicate particles appear at grain boundary triple points. These form as a result of the relatively high oxygen contents found in the Nb_5Si_3 sputtering targets used to manufacture the microlaminates. The fourth limitation is that on annealing the Nb/Nb_5Si_3 microlaminates at or above 1500°C, a metastable Nb_3Si interfacial phase forms (Figure 1(a)). While no equilibrium Nb_3Si phase is predicted at this temperature, its stress-induced formation may have ramifications regarding the long-term microstructural stability of these materials.

On the basis of these observations our approach was to investigate several new processing routes as well as to improve our existing processing methods.

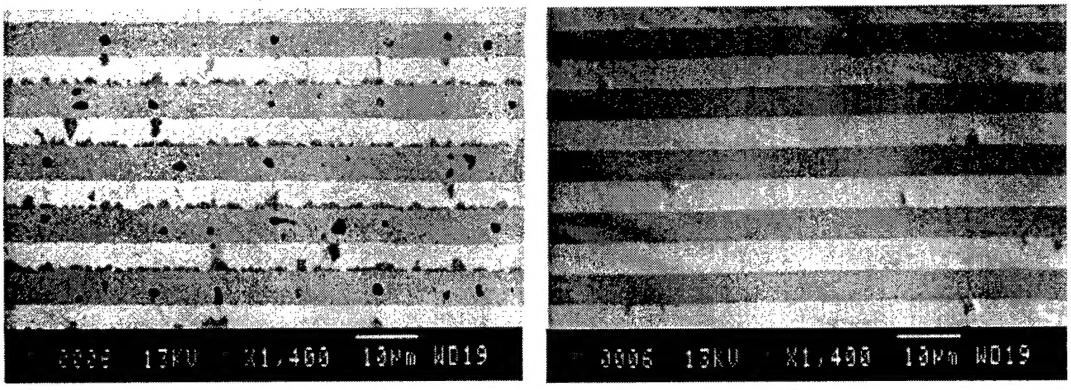


Figure 1: (a) SEM micrograph of Nb/Nb_5Si_3 microlaminate after annealing in vacuum at 1500°C for three hours. The light grey layers are Nb_5Si_3, the light layers are Nb, and the dark grey regions are a metastable Nb_3Si phase that forms in the Nb layers on cooling. (b) SEM micrograph of Nb/Nb_5Si_3 microlaminate after annealing under pressure at 1500°C for three hours. The light grey layers are Nb_5Si_3, and the light layers are Nb. No metastable Nb_3Si phase appears in the Nb layers and no porosity appears in the silicide phase.

<u>Improvements to the Existing Processing Route:</u>

In order to suppress the formation of porosity in the Nb/Nb_5Si_3 microlaminates we investigated hot pressing during high temperature anneals. As can be seen from figure

1(b), this was an extremely effective approach to suppressing the formation of porosity, with no apparent bulk porosity after annealing at 1500°C for 3 hours, or indeed after annealing at 1600°C for 3 hours. However, even after the latter heat treatment the silicide grain size was still only on the order of 1μm.

In addition to removing porosity, hot pressing also eliminated the Nb_3Si metastable interfacial phase. As discussed previously, a metastable Nb_3Si interfacial phase forms when the Nb/Nb_5Si_3 microlaminates are annealed at or above 1500°C. However, by annealing the microlaminates at 1500°C under a 100MPa compressive stress we were able to suppress the formation of this phase (compare Figures 1(a) and (b)). This result agrees with our report that the formation of the Nb_3Si phase is favored by the tensile stresses that arise in the Nb layers on cooling for high temperature anneals [4-6].

While hot pressing was successful in suppressing porosity formation and metastable phase formation, the average grain size on all of these microlaminates never exceeded 1 μm. In order to increase the grain size, three new processing routes were investigated. These were (1) vapor deposition onto a heated substrate, (2) annealing under a large thermal gradient, and (3) hot pressing of Nb/Si composites that were formed from sheet material or vapor deposited from very pure elemental targets.

Vapor Deposition at Elevated Temperatures

We investigated vapor deposition onto heated substrates as a technique for depositing *crystalline* Nb_5Si_3. By avoiding the deposition of amorphous Nb_5Si_3 we hoped to eliminate much of the subsequent densification associated with the crystallization and growth of the Nb_5Si_3 phase, thereby eliminating one of the largest potential sources for the formation of pores in the silicide layers.

We sputter deposited Nb_5Si_5 directly onto substrates heated to 300°C, 400°C and 600°C and compared them to Nb_5Si_3 deposited on an unheated substrate. X-ray diffraction of the deposited samples revealed that the Nb_5Si_3 phase produced a diffuse peak (full width half max (2θ) of 6 degrees) that did not narrow significantly with increasing deposition temperature. This suggests that most of the Nb_5Si_3 layer is still amorphous or at least fine grained, even at these high deposition temperatures. Rawal et al [7] have shown that depositing at 750°C resulted in crystalline Nb_5Si_3. However, this temperature range could not be obtained in our current deposition chamber. Given this technical limitation, and the fact that the grain structures reported by Rawal et al were columnar in nature, (and offer poor mechanical properties), further investigations into this method of enhanced processing were discontinued.

Annealing Under a Large Thermal Gradient

Baker et al [8] have shown that discontinuous grain growth occurs during the recrystallization of Cu under a large thermal gradient. We investigated whether the crystallization of the Nb_5Si_3 would exhibit a similar response to large thermal gradients.

A series of anneals were carried out using an image furnace in collaboration with Dr. Ian Baker at Thayer School of Engineering. The samples were drawn though a chilled block into the main heating region of the image furnace. We conducted a series of experiments with peak temperatures ranging from roughly 1000°C to the melting point of the alloy (roughly 2500°C). We found no significant increase in the grain size of the silicide over conventional processing route. Indeed in one of the samples, the silicide melted and decomposed into a two-phase region (presumably Nb_5Si_3 and Nb_3Si) in which the average grain size was still only several microns. In addition, considerable bulk porosity developed in the samples, presumably due to the evolution of gaseous Si from the silicide layers. Given the lack of success in growing the silicide grains, this method was abandoned.

Hot Pressing of Nb/Si Microlaminates.

In our initial studies of manufacturing Nb/Nb_5Si_3 microlaminantes we attempted to manufacture Nb_5Si_3 layers by interdiffusion of elemental Nb and Si layers at elevated temperatures after an initial sputter deposition. However, the elemental layers delaminated extensively along the Nb/silicide interfaces due to stresses resulting from densification. Thus processing using hot pressing was investigated.

W. Provancher and A.K. Ghosh [9] showed that hot pressing sheets of Nb and Si at 1650°C for 3 hours at a pressure of 27.6MPa produced Nb_5Si_3 with a grain size of roughly 20 microns. We reported previously that hot pressing Nb/Si microlaminates at 10MPa for 3 hours produced microlaminates with no evidence of delamination, though silicide grain sizes were still limited to ~1μm at these temperatures. In order to fundamentally understand the kinetic and physical limitations of the process (and more closely reproduce Provancher and Ghosh's experiments) we repeated their experiments by hot pressing sheets of Nb and sheets of Si. This was performed using a series of anneals on 120μm sheets of Si sandwiched between 100μm sheets of Nb. Hot pressing experiments were conducted at a pressure of 10MPa and temperatures of 1300°C, 1565°C, 1600°C, 1635°C and 1670°C. The lowest temperature was chosen to be below the melting point of Si (1410°C) while the highest temperatures were chosen to straddle the reported phase stability limit in the system at 1660°C.

After hot pressing at 1300°C, Si remained at the center of the trilayer but there was substantial silicide formation. In addition, at the interface between the remaining Si and the silicide, an oxygen-rich contamination layer was present. After annealing at higher temperatures, the Si layer was no longer present, but the remnants of the contamination layer were still present in the center of the silicide layers (Figure 2). Chemical analysis of the microlaminate showed that in addition to Si layers, $NbSi_2$ and Nb_5Si_3 layers were also present [10].

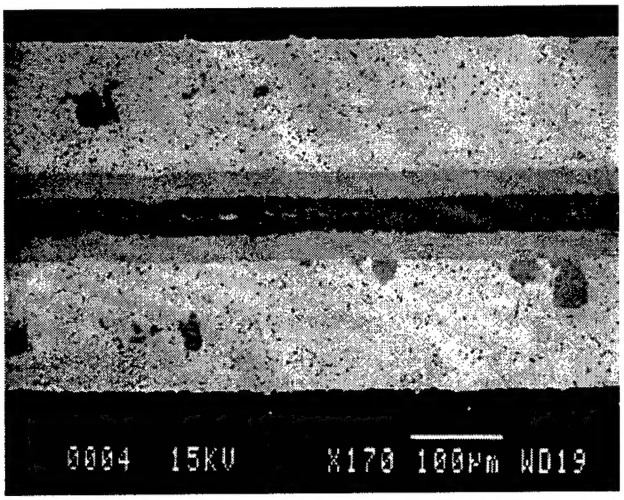
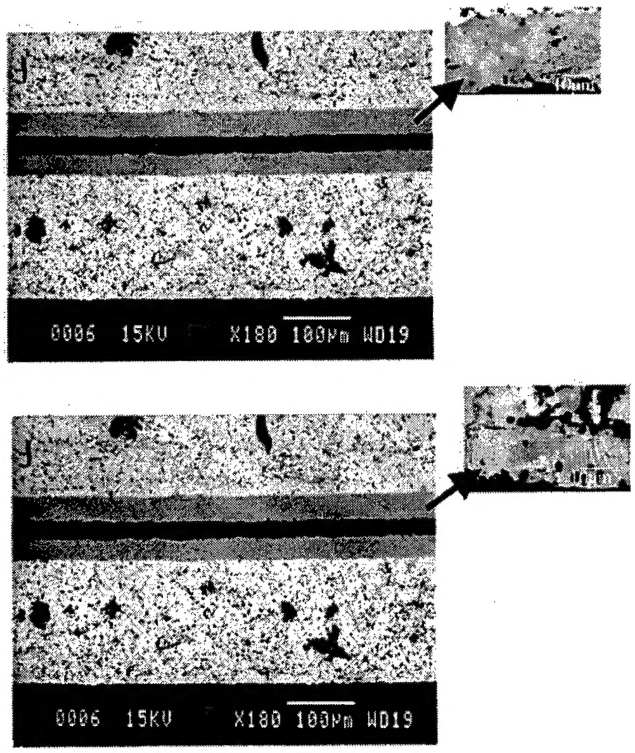


Figure 2: SEM micrograph of Nb/Nb_5Si_3 trilayer laminate after 3 hours at 1565^0C under 10MPa [10].

On annealing at higher temperatures the Nb_5Si_3 layers consumed the $NbSi_3$ layers. After annealing at 1300°C, the Nb_5Si_3 layer was 4.9µm thick, on annealing at 1565°C it was 27µm thick, after 1600°C it was 32µm (Figure 3(a)), after 1635°C it was 34µm (Figure 3(b), and after 1670°C it was 38µm thick (Figure 3(c)). In addition the average grain size of the silicide increased from 3µm at 1565°C to roughly 10µm after both the 1635°C and 1670°C anneals. The 1635°C and 1670°C anneals, however, were accompanied by phase segregation in the Nb_5Si_3 layers [10].



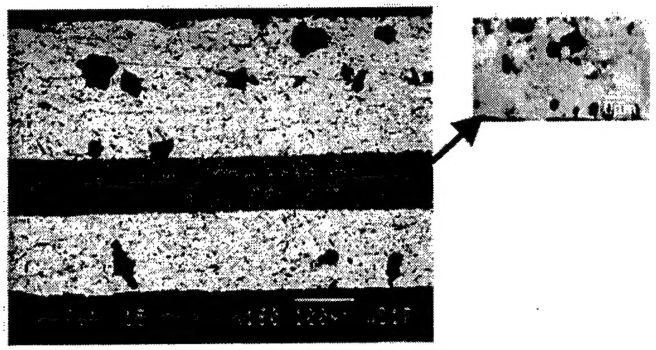


Figure 3: SEM micrograph of Nb/Nb_5Si_3 trilayer laminate after annealing at (a) 1600°C, (b) 1635°C, and 1670°C. The silicide layers were 32μm, 34μm, and 38μm thick, respectively, while the average grain size of the silicide phase increased from 3μm at 1565°C to roughly 10μm after both the 1635°C and 1670°C anneals [10].

Examination of the Nb_5Si_3 grains in the samples hot pressed at 1635°C and 1670°C (Figure 3 (b) and (c)) reveals a "feathered" microstructure indicating that the Nb_5Si_3 has phase segregated. Notice that the breakdown occurred preferentially in the $NbSi_2$-side of the Nb_5Si_3 and proceeded further into the Nb_5Si_3 layer on annealing at higher temperatures. The precise breakdown mechanism was not investigated, but for practical purposes it suggests that hot pressing needs to remain below 1635°C to retain single-phase Nb_5Si_3 layers.

It is apparent from Figure 3 that the amount of porosity in the Nb_5Si_3 layers increased with increasing hot pressing temperature. The fact that this porosity was predominantly at the interfaces strongly suggests that it is Kirkendall porosity, as would have been expected by the nature of this interdiffusion reaction [10].

These experiments indicate that hot pressing sheets of Nb and Si suffers from an interfacial contamination phase that is retained throughout the experiments, limiting the quality of the films that one can produce. Furthermore, in spite of the high pressure during processing, considerable porosity is present in the silicide layers, even after hot pressing at high temperatures. Nevertheless, after 3 hours at 1600°C we were able to generate a Nb_5Si_3 layer with a grain size of roughly 8μm, eight times greater than what we obtained from the foils made from composite Nb_5Si_3 sputtering targets after similar anneals.

As a final processing alternative we vapor deposited microlaminates with elemental layers of Nb and Si and then hot pressed the films. This strategy produced microlaminates with a higher purity than is possible by sputtering from composite Nb_5Si_3 targets or by simply hot pressing sheets of Nb and Si. An example of such a film after annealing at 1500°C for 3 hours is shown in Figure 4 [11]. As can be seen the films, the elemental layers have reacted completely after hot pressing at 1600°C. Grain size measurements indicate that the silicide grain size is 6μm, similar to that seen in the hot pressed sheet experiments. Surprisingly, there was no bulk porosity in these films after

annealing. Initial experiments also suggest that the silicide is now free of a silicate phase. Additional efforts will be needed to capitalize on this promising processing method.

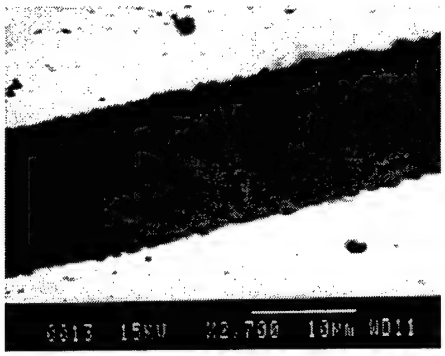


Figure 4: SEM micrograph of a Nb/Si microlaminate vapor deposited from elemental targets and then annealed under pressure at 1500°C

5.2 High Temperature Properties of Nb/Nb_5Si_3 Microlaminates

High temperature plastic deformation has been studied for many years using course-grained metals and ceramics, and a strong understanding of such deformation has been established [12]. Knowledge of plasticity and creep in microlaminates and fine-grained materials, however, is still rather limited, due in part to experimental challenges. Creep studies of microlaminates are subject to layer breakdown and pinch-off at the high temperatures. Similarly, fine-grained systems can be subject to grain growth during testing. Without a stable microstructure, clear identification of deformation mechanisms is very challenging [13-14].

Through a careful choice of materials systems, though, one can produce microlaminates samples with layers and grain structures that are chemically and physically stable during high temperature testing [15-16]. In addition, standard, bulk tension techniques can be used to test the samples because, while the individual layers in a laminates may be just micrometers thick, the layered foil can have a total thickness ranging from 20 to 200μm. Such high values of total thickness permit the films to be removed from their substrates for testing as freestanding specimens, and their microstructures are stabilized by the fine layering within the foils, assuming the layers are chemically stable at temperature [15-16]. Ease of characterization and study can be superior even to that of bulk specimens, because the grain size of some phases can be controlled throughout the creep test by the thickness of the deposited layers, particularly after annealing at high temperatures to stabilize the grain structure.

To study plastic and creep deformation in Nb/Nb_5Si_3 samples, two sets of samples were fabricated. First, Nb/Nb_5Si_3 microlaminates were fabricated for testing. In these samples the high melting temperature silicide layers dominate deformation at or above 1000°C. Plasticity and creep deformation are controlled by deformation within the silicide layers. Thus, for these specimens we focus on the grain sizes of the silicide layers. The much

softer Nb layers offer little resistance to deformation and therefore do not impact the stress – strain rate relationships. To understand how Nb deforms in thin layered and fine grained structures, a second set of samples were fabricated for testing: Cu/Nb microlaminates. In these samples the Cu layers are the much softer phase at high temperature so the Nb layers control deformation and determine stress – strain rate relationships. Thus, the properties of fine-grained Nb can be investigated by testing Cu/Nb microlaminates at high temperatures.

Properties of the Nb_5Si_3 Phase:

Two sets of Nb/Nb_5Si_3 microlaminate samples were fabricated. One contained silicide layers with a 0.2μm grain size and the other contained silicide layers with a 0.3μm grain size. The samples measured 60μm in total thickness and 5mm and 50mm in width and length. The individual layers were 5.0μm or 10.0μm thick, depending on the sample. The samples were tested in tension in argon at 1000°C and 1100°C. Constant loads were applied until steady state creep rates were obtained and then the loads were increased to obtain a range of stress-strain rate relationships. One example of raw test data is shown in Figure 5. Note that six different loads were applied and in each case, a steady state creep rate was obtained. The resulting stress-strain rate data are plotted along with other sets in Figure 6(a) and (b). Figure 6(a) shows data at two different temperatures (1000°C and 1100°C) for the 0.2μm grain size. Strain rates increase with temperature, as expected, and the stress exponent is near 1.0 for both temperatures, suggesting a diffusional creep mechanism is controlling deformation. As grain size increases by 1.5x in Figure 6(b) to 0.3μm, the strain rate drops by more than 10x. This suggests strong grain size dependence, near $1/d^3$, as expected for Coble Creep. However, on shifting to the 0.3μm grain size, the stress exponent appears to increase towards three suggesting a shift to power law creep at the larger grain sizes.

Figure 7 shows strain rates at various temperatures for a Nb/Nb_5Si_3 microlaminate with a 0.2μm silicide grain size. The applied stress is 1.5 MPa and the measured activation energy is 226 kJ/mol. The value for bulk diffusion in Nb_5Si_3 is 235 kJ/mol. This suggests that bulk diffusion is controlling the diffusional creep, not grain boundary diffusion as one might expect for this fine grain size. However, diffusion in fine-grained samples is not well understood and little data exists [12-14]. Additional studies are needed.

Figure 8 compares creep of the Nb/Nb_5Si_3 microlaminates with other Nb silicide composites, including monolithic Nb_5Si_3. All tests were performed at 1100°C. Note that the creep rate for the microlaminates drops considerably by enlarging the silicide grain size suggesting that more significant increases in grain size could lead to creep rates comparable to the in-situ composites. A grain size of 5μm in the silicide phase is likely to demonstrate acceptable creep rates at 1100°C. Such behavior justifies additional efforts to further develop the deposition and hot pressing of Nb/Si microlaminates as a method to fabricate Nb/Nb_5Si_3 microlaminates with larger silicide grain structures.

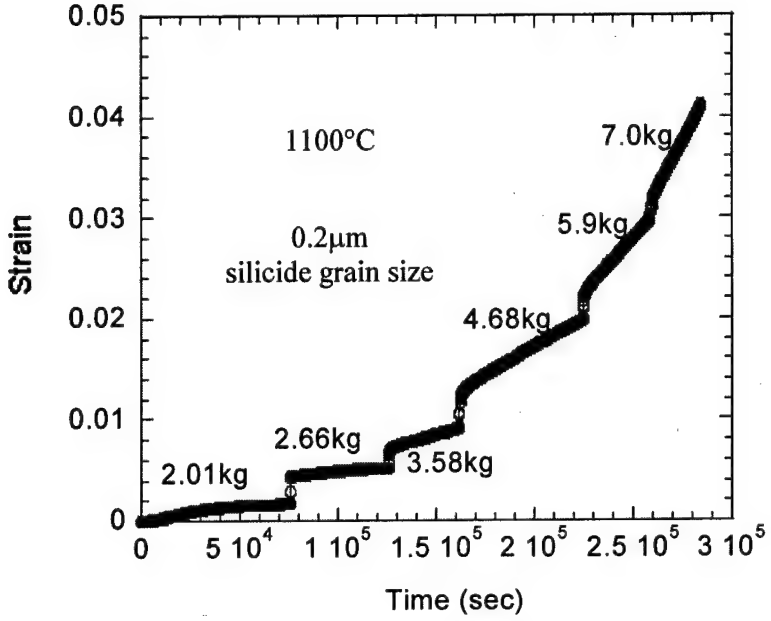


Figure 5: Strain is plotted versus time for a tensile creep test of a Nb/Nb_5Si_3 microlaminate with a 0.2μm silicide grain size. The test was conducted in argon at 1100°C. A constant load was applied until a steady state creep rate was obtained and then the load was increased to obtain a range of stress-strain rate relationships.

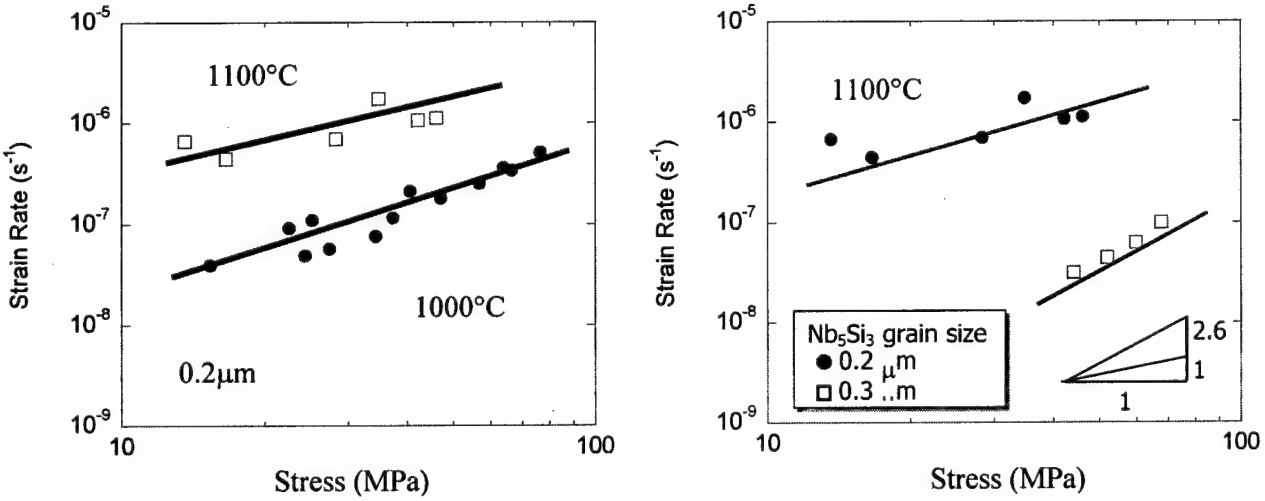


Figure 6: (a) Strain rate is plotted versus stress for tensile creep tests of a Nb/Nb_5Si_3 microlaminate with a 0.2μm silicide grain size. The tests were conducted in argon at 1000°C and 1100°C. Note the linear dependence of creep rate on stress and the strong dependence on temperature. (b) Strain rate is plotted versus stress for tensile creep tests of Nb/Nb_5Si_3 microlaminates conducted in argon at 1100°C. The samples with a 0.3μm silicide grain size show a far lower creep rate suggesting a strong inverse dependence of creep rate on grain size.

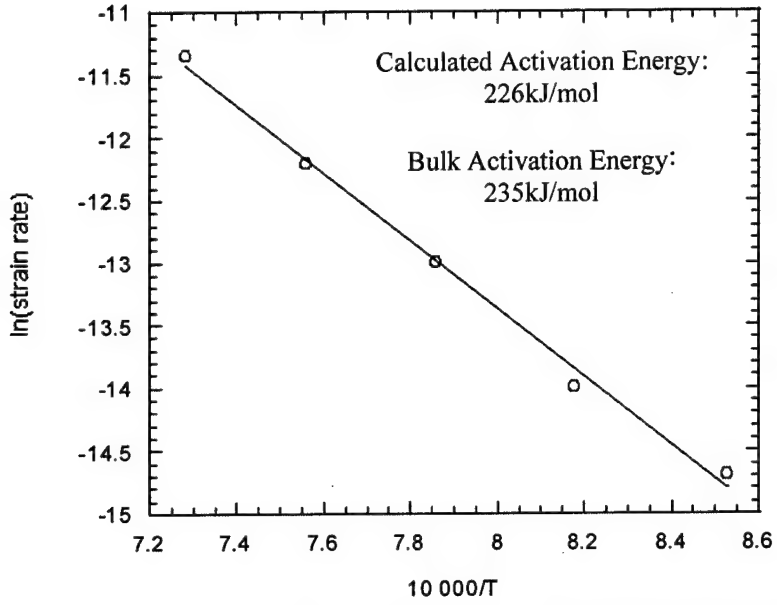


Figure 7: Natural log of strain rate plotted versus inverse temperature for tensile creep tests of a Nb/Nb_5Si_3 microlaminate with a 0.2μm silicide grain size. The tests were conducted in argon at an applied stress of 1.5MPa. Note that the measured activation energy is close to the value for bulk diffusion in Nb_5Si_3.

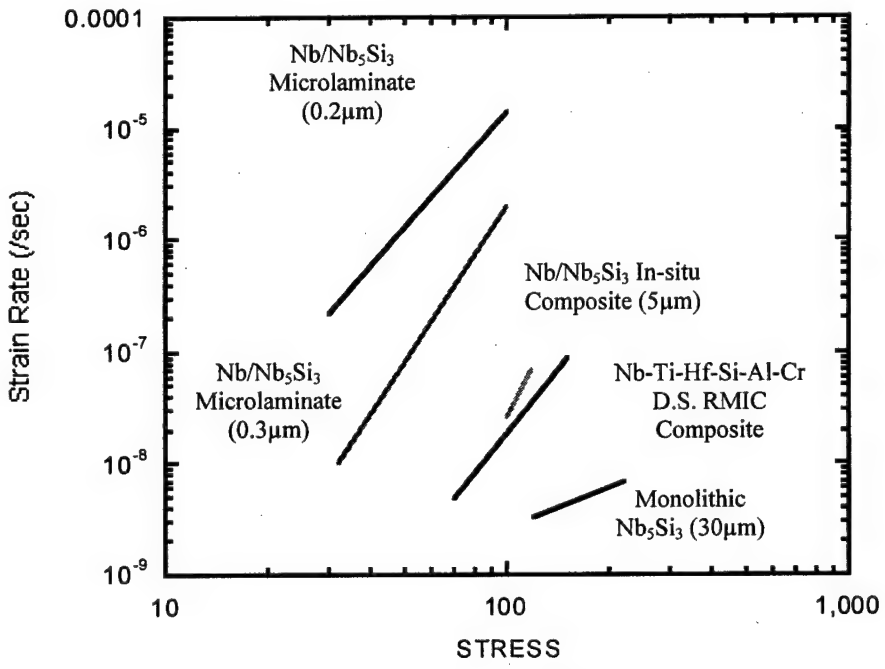


Figure 8: Strain rate is plotted versus stress for tensile creep tests of various Nb-based composites, including monolithic Nb_5Si_3. All tests were performed at 1100°C. Note that the creep rate drops considerably by enlarging the silicide grains size in the microlaminate samples suggesting that more significant increases in grain size could lead to creep rates comparable to the in-situ composites.

Properties of the Nb Phase

Similar to the Nb/Nb_5Si_3 microlaminates, copper and niobium were sputter deposited with bilayer thicknesses varying from 1 μm to 10 μm and total thicknesses of 100 μm as listed in Table 1. Figure 9 is a cross-sectional SEM micrograph of an as-deposited Cu/Nb 1μm/1μm foil. After annealing the Cu layers have a strong <200> texture Cu , the Nb layers have a strong <110> texture and all grains are columnar and equiaxed.

Table 1: Specifications and annealing conditions for Cu/Nb specimens.

Sample Label	Cu Layer Thickness (μm)	Nb Layer Thickness (μm)	Total Foil Thickness (μm)	Anneal Temp (°C)	Anneal Time (hrs)
500/500	0.5	0.5	100	800	3
1/1	1.0	1.0	100	800	8
2.5/2.5	2.5	2.5	100	800	24
5/5	5.0	5.0	100	900	24
1/5	1.0	5.0	60	900	24

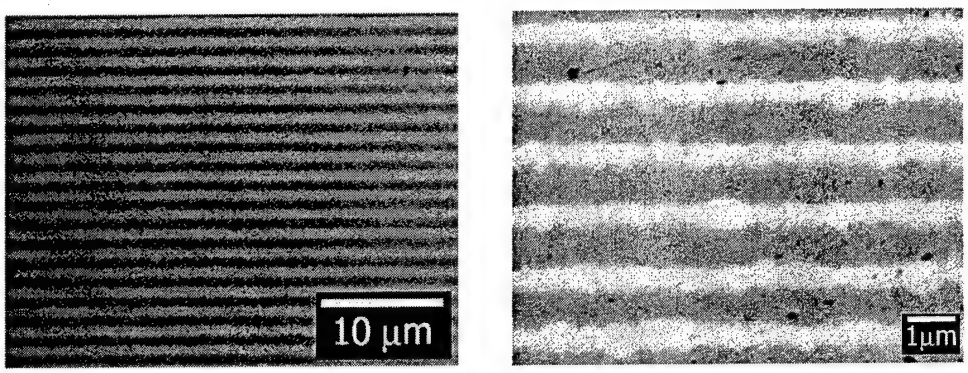


Figure 9: Cross-sectional SEM micrograph of as-deposited Cu/Nb 1μm/1μm foil. The darker layers are Cu and the lighter layers are Nb.

In the first part of this study of Cu/Nb multilayers uniaxial tensile tests were performed to determine the stress at which plastic deformation begins in these foils, and to investigate grain boundary strengthening effects as a function of temperature and strain rate.

Based on a series of tensile tests, grain boundary strengthening is apparent at room temperature [16]. The yield strength of the Cu/Nb multilays followed a Hall-Petch relationship at room temperature with a slope (k_{RT}) of 156 ± 26 MPa·$\mu m^{1/2}$ and an intercept (σ_0) of 168 ± 25 MPa (Figure 10). Tests on samples with a different ratio of Cu and Nb layer thicknesses revealed that Nb layers offer most of the resistance to plasticity at room temperature, and an increase in Nb volume fraction results in an increase in yield strength according to an isostrain model [16].

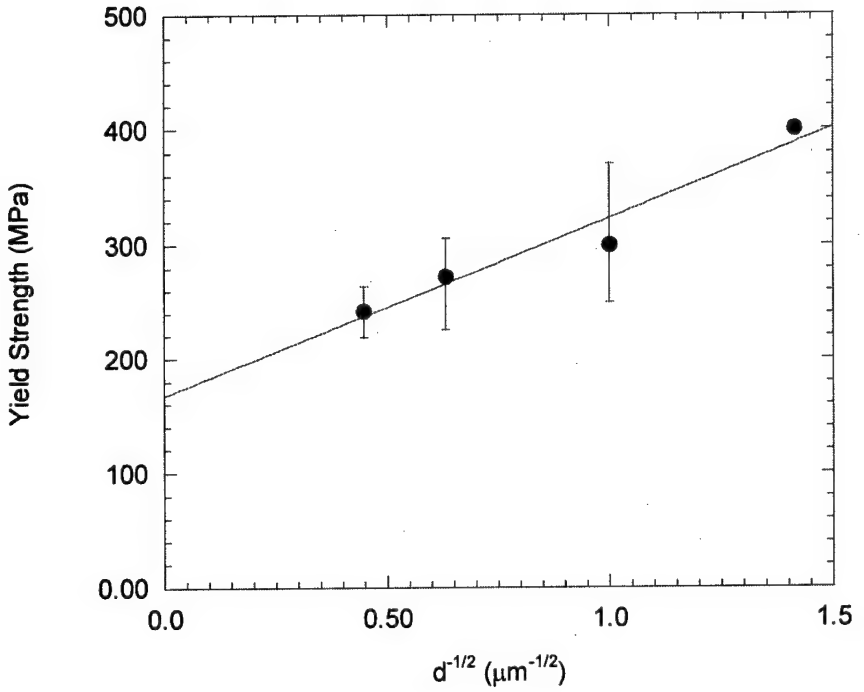


Figure 10: Hall-Petch plot for Cu/Nb foils tested at room temperature. Stresses were calculated considering the entire specimen cross-sectional area. The slope (k_{RT}) is 156 ± 26 MPa·$\mu m^{1/2}$ and the intercept (σ_0) is 168 ± 25 MPa.

Grain boundary strengthening was also observed at elevated temperatures but at 600°C the Nb layers bear almost all of the applied load. Thus, stresses were calculated based on the Nb cross-sectional area. At 600°C and a strain rate of 10^{-4} s^{-1}, the Hall-Petch slope for Nb has a value of 178 ± 27 MPa $\mu m^{1/2}$ and the intercept 122 ± 26 MPa as shown in Figure 11. The Hall-Petch slope decreases as strain rate is lowered, indicating that time-dependent plasticity is active. Due to the time-dependent plasticity, no grain boundary strengthening is expected at strain rates below 10^{-6} s^{-1}.

To study the creep deformation of Nb, the Cu/Nb multilayers were tested under constant load conditions at 600°C. Due to the fact that Cu creeps 10^6 times faster than Nb at this temperature, the study effectively quantified creep rates in fine-grained Nb. Figure 12 shows stress vs. strain rate for films with four different Nb grain sizes. For these specimens with grain sizes ranging from 0.5 μm to 5 μm, two distinct regimes were observed – Power Law creep at high stresses, and an interface-controlled creep mechanism at lower stresses. Figure 13 shows stress vs. strain rate for Cu/Nb foils with grain sizes of 1 μm and 5 μm. This figure illustrates the lack of grain size dependence at high stresses, and the reciprocal grain size dependence at low stresses. Table 2 lists measured activation energies for creep in these specimens, along with previously measured values for relevant processes [16,17].

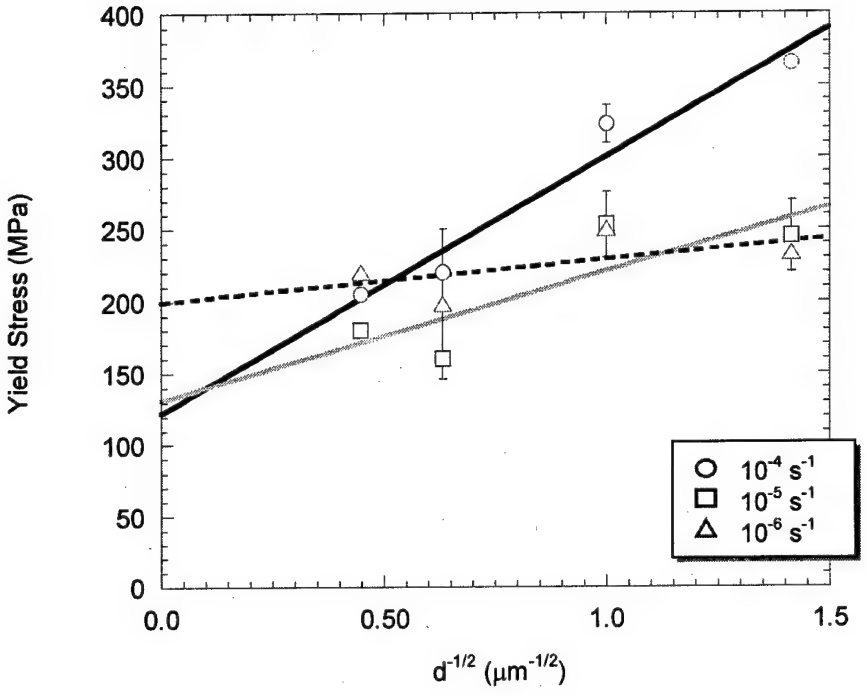


Figure 11: Hall-Petch plot for Cu/Nb foils tested at three strain rates at 600°C. Stresses were calculated considering the effective area (Nb layers only). The Hall-Petch slope decreases as strain rate decreases.

At high stresses, the stress dependence (power law exponent) increased with increasing grain size, with an average value of 3.5. Though the power law exponent has a slight grain size dependence, the values of creep rate in this regime had no apparent dependence on grain size. Measured activation energies are consistent with the mechanisms for Power Law creep, and it was concluded that Power Law creep is the dominant deformation mechanism in this regime [16,17].

At low stresses, creep rates exhibited a linear dependence on stress, and the measured activation energy was consistent with that for the generation of vacancies at Nb grain boundaries. This behavior is inconsistent with the model of interface-controlled creep given by Burton [18], which predicts a higher stress dependence of creep rate and higher activation energy than what is observed. Consideration of a simple model for creep in which vacancy generation at the grain boundaries is the rate-controlling mechanism, however, reveals dependences of creep rate on both applied stress and grain size, consistent with those observed [16,17]. In addition, the thermally-activated rate-controlling process for this model is the generation of vacancies at grain boundaries, also consistent with the observed values. The dependence of strain rate on grain size at low stresses is consistent with this model's predictions for interface-controlled creep. For the range of grain sizes tested, which spans an order of magnitude, the strain rate scales as $\dot{\varepsilon} \propto 1/d$. Based on the model presented here for vacancy generation at grain boundaries,

it can be concluded that an interface-controlled creep mechanism dominates deformation in this regime [16,17].

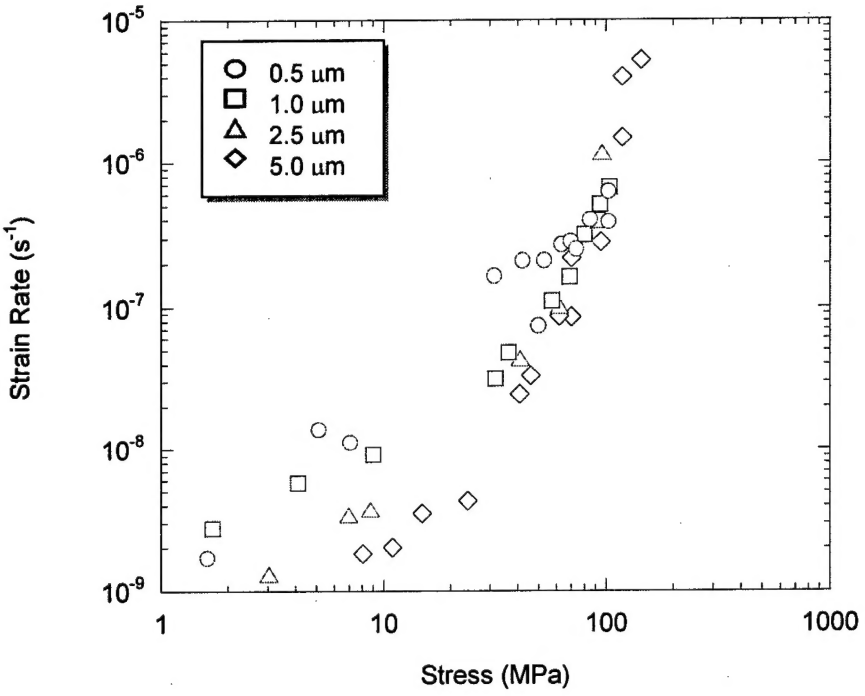


Figure 12: Stress vs. strain rate for Cu/Nb foils tested at 600°C.

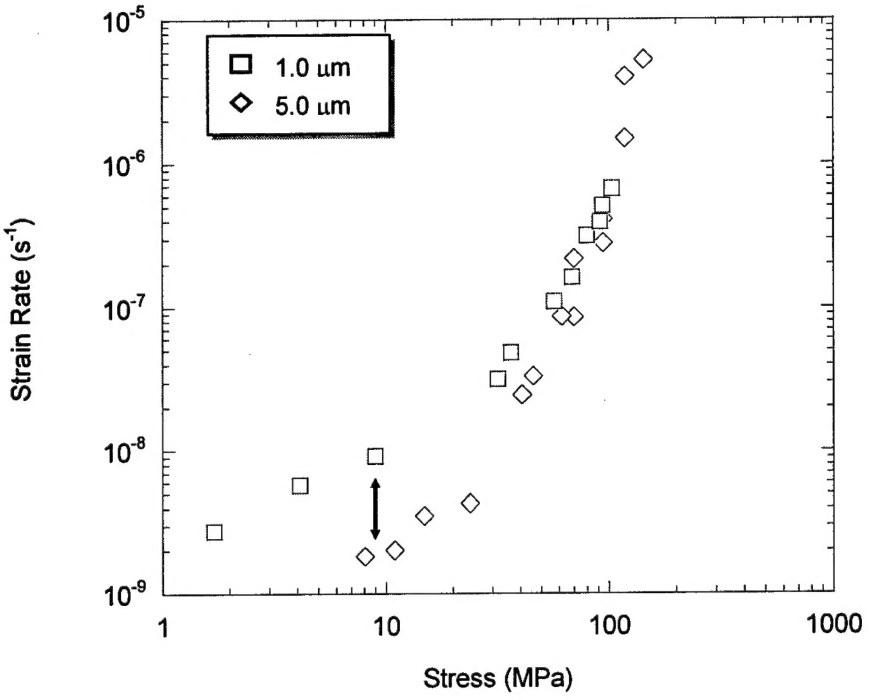


Figure 13: Stress vs. for Cu/Nb 1 μm and 5 μm foils tested at 600°C.

Table 2: Activation energies for creep and relevant processes in Nb [16].

Mechanism	Activation Energy [kJ/mol]
Self-diffusion	439
Lattice (Bulk) Diffusion	401
Boundary Diffusion	263
Core Diffusion (Power Law Creep)	263
Creep, High Stress	288± 22
Vacancy Generation, Nb Bulk	296
Vacancy Generation, Nb grain boundary	148
Creep, Low Stress	140± 27

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